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# A comparative mass spectroscopic study between infrared and ultraviolet laser ablation of a superconducting $YBa_2Cu_3O_{7-x}$ target

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**Abstract**

Time-of-flight mass spectra of ionic species produced by the laser ablation of a $YBa_2Cu_3O_{7-x}$ target have been measured. The experimental geometry and laser conditions used in this study are similar to those used for the deposition of thin films by laser ablation. A comparison of the mass spectra by using both an infrared laser and an ultraviolet laser as irradiation sources, provides valuable information regarding the identification of the species responsible for the growth of thin films. In the case of the infrared laser both light- and heavy-mass species are observed. In the case of the ultraviolet laser, only metal ions and their oxides are observed. Oxygen introduced with a pulsed nozzle near the plume enhances the formation of oxides. It is suggested that these oxides provide the means by which the oxygen is transported to the substrate. (Int J Mass Spectrom 189 (1999) 1–7) © 1999 Elsevier Science B.V.

*Keywords:* Mass spectrometry; Time of flight; Laser ablation; Plasma; Superconductivity

## 1. Introduction

The pulsed laser deposition (PLD) technique has been used with success in growing good quality thin films of several multicomponent materials, and particularly, of the ceramic compounds with high superconducting transition temperature such as $YBa_2Cu_3O_{7-x}$ (YBCO). The great advantage of PLD is the relative ease of how it can be realized in the laboratory. A large number of attempts have been made to understand the multistage mechanism of the extremely complicated process of depositing material with the correct stoichiometry [1].

Several experimental studies have investigated the species in the plasma plume created above a YBCO target. Berardi et al. [2] used time-of-flight (TOF) mass spectroscopy to investigate the formation of positive ions in the plasma plume created by a XeCl laser (308 nm) in vacuum and in oxygen environments. The authors claim that their experimental geometry allows the investigation of the plume composition as a function of distance from the surface of the target. They report the emission of heavy species and YBCO clusters.

A quadrupole mass spectrometer was used by Chrisey et al. [3] to measure the mass and energy

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distribution of neutral species ejected in the laser evaporation of a YBCO target by a KrF laser (248 nm). Contrary to [2], their mass spectra contain peaks only of metal atoms and their common oxides. They also report that a large population of these species has energies greater than 10 eV.

Becker and Pallix [4] used a reflecting TOF mass spectrometer to investigate the mass distribution of positive ions produced from 1064 nm plus 532 nm laser ablation of a YBCO target. They report significant emissions of very low-mass ions and clusters with masses ranging from $10^3$ up to $10^6$ atomic mass units (amu) up to the laser fluences ($\sim$3.4 J cm$^{-2}$) required to visually observe a plume of white light; at higher fluences, large-mass clusters essentially disappear while low-mass ion intensities continue to grow.

In this article we report on a systematic study of the time-of-flight mass spectra of positive ions in the plasma plume created by the laser ablation of a YBCO target. The mass spectra are acquired in vacuum and in oxygen—introduced near the plume with a pulsed-nozzle—for two different radiation wavelengths. Also, preliminary data from a two-laser experiment are presented that lend support to the arguments used in explaining our observations.

## 2. Experimental method

The molecular beam apparatus used is the same employed previously [5,6] to perform experiments on cluster formation and stability. Therefore, only a short description of the main components is given here. The apparatus consists of three differentially pumped chambers: the ablation, the acceleration, and the detection ones. In the ablation chamber, plasma is produced through the interaction of a laser beam at an angle of 45° with a rotating solid target. The target is a home-prepared pellet of the superconducting compound YBCO with $T_c = 92$ K.

The expanding plasma plume enters via a skimmer orifice (4 mm diameter) in the acceleration chamber where a pulsed double field acceleration unit directs the ions through a 6 mm collimator toward the third chamber that houses the detection assembly for the TOF analysis of the produced ions. The ions are measured with two microchannel plate (MCP) detectors by using two different operation modes, the linear and the reflecting. In the first case the MCP can be inserted externally (through a vacuum translator) perpendicular to the spectrometer axis, and in the latter case the MCP is placed off-axis in order to measure the backwards reflected ions from the reflecting assembly. In both cases, the MCP output is directly connected to a computer controlled digital storage oscilloscope, where the TOF mass spectra are acquired and stored shot by shot. The spectra that will be discussed are obtained by averaging several (about 500) single shot spectra.

For investigating the effects of the molecular-oxygen presence in the plasma plume we use a pulsed nozzle with an orifice of 1 mm diameter. The nozzle is placed 10 mm above the ablation point and 5 mm away from the target's surface. The assembly of the rotating target and the nozzle can be positioned such that the plasma expands collinear or perpendicular to the TOF spectrometer axis. With no oxygen in the nozzle the pressure in the three successive vacuum chambers is $3 \times 10^{-6}$, $10^{-6}$, and $2 \times 10^{-7}$ mbar, respectively, and when the $O_2$ nozzle operates with a 3 bar inlet pressure, the pressure in the three successive chambers is $10^{-4}$, $10^{-6}$, and $5 \times 10^{-7}$ mbar, respectively. The inlet pressure of the oxygen is chosen so that in the plasma–oxygen interaction region ($\sim$10 mm away from the nozzle orifice) the local pressure is $\sim$0.3 mbar. The local pressure is estimated by taking into account the pressure drop across the supersonic jet streamline resulting from the isentropic expansion of a diatomic gas with a heat capacity ratio $\gamma = 7/5$ [7]. The experimental geometry used in the TOF investigations is similar with that used for the deposition of thin films.

Two different laser sources are used: a KrF excimer laser (248 nm) and the fundamental of a Nd:YAG laser (1064 nm). The laser beam is focused by a lens with a focal length of 50 cm onto the rotating target; the area of the laser spot is 2.8 mm$^2$ for the excimer and 0.5 mm$^2$ for the infrared laser.

The *Q*-switched Nd:YAG laser used for the target ablation, was developed in our laboratory. The laser

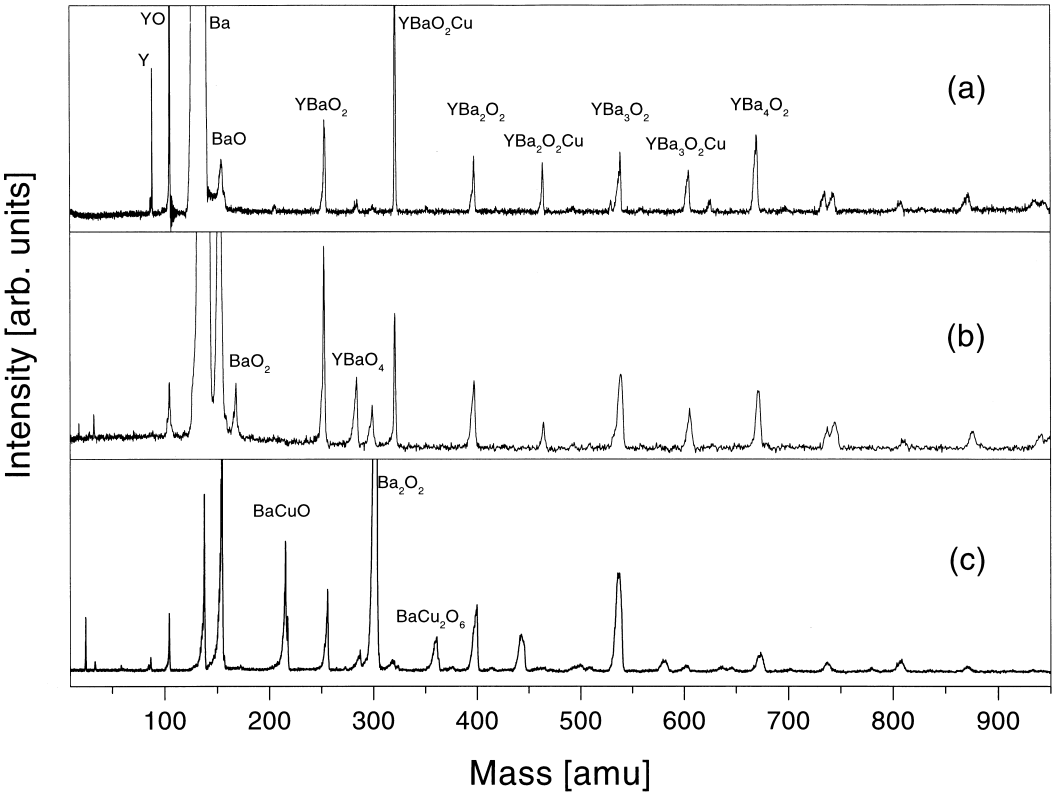


Fig 1. TOF mass spectra of positive ions in the plasma plume produced by the ablation of a YBCO target with a Nd:YAG laser (fluence of 1 J $cm^{-2}$). The spectra were obtained with the linear detection mode both in (a) vacuum, and in oxygen with the pulsed nozzle aligned either (b) perpendicular or (c) parallel to the spectrometer axis.

pulse has a 15 ns [full width at half maximum (FWHM)] duration, and its energy can be adjusted from 50 to 300 mJ per pulse. The excimer laser used is a commercial one (Lambda Physik Compex 110) with a 25 ns pulse width and its energy can be varied from 80 to 300 mJ per pulse.

## 3. Results

### *3.1. Infrared laser*

Fig. 1 illustrates typical TOF mass spectra of cations produced by the impingement of laser pulses from a Nd:YAG laser with a repetition rate of 10 Hz and laser fluence of 1 J $cm^{-2}$ on the surface of a YBCO pellet. The spectra are obtained with the linear detection mode both in vacuum (a), and in oxygen with the pulsed nozzle aligned either perpendicular (b) or parallel (c) to the spectrometer axis. Although species with mass up to 2000 amu are observed, the data shown in Fig. 1 extend only up to 900 amu. The mass resolution of the spectrometer ($M/\Delta M \approx 350$ at $M = 250$ amu) is sufficient to resolve isotopes of the cations, thus permitting the identification of most of the peaks with high certainty.

The most intense ion signals in vacuum [Fig. 1(a)] are atomic (Y and Ba), monoxide (YO and BaO) and oxide clusters. Two series of clusters have been identified: (1) $YBa_nO_2$ and (2) $YBa_nO_2Cu$ with $n \geq 1$. Even though no atomic or monoxide species of Cu are observed, Cu is part of the oxide clusters $YBa_nO_2Cu$.

In the presence of oxygen, introduced by the nozzle aligned perpendicular to the spectrometer axis, the mass spectra [Fig. 1(b)] are slightly different from

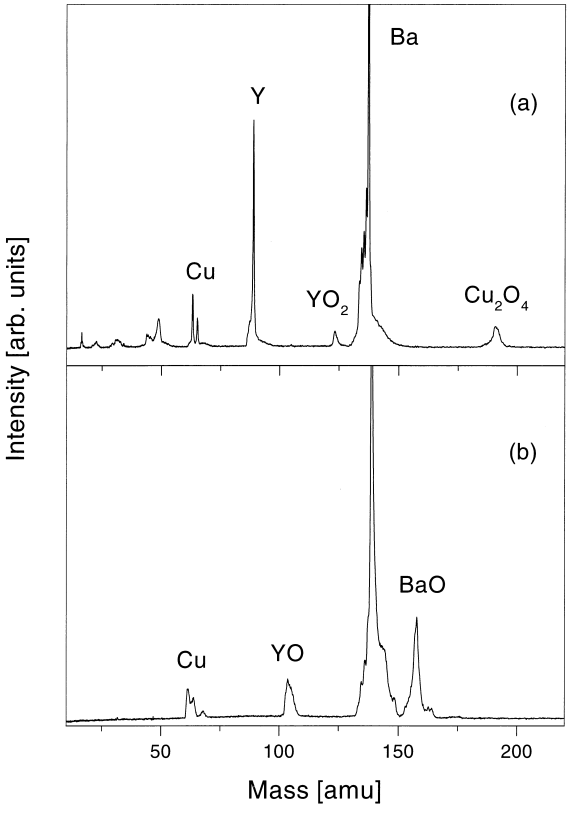


Fig. 2. TOF mass spectra of positive ions in the plasma plume produced by the ablation of a YBCO target with a KrF laser (fluence of 1.2 J $cm^{-2}$). The spectra were obtained with the reflecting detection mode both in (a) vacuum, and in (b) oxygen with the nozzle aligned perpendicular to the spectrometer axis.

those obtained in vacuum. A few new peaks, mainly because of oxygen, are observed, e.g. $O_2$ and $BaO_2$, whereas the Y peak disappears.

By altering the experimental geometry and aligning the nozzle parallel to the spectrometer axis the main features of the spectrum remain, and furthermore a new series of peaks emerges, which is due to clusters of the type $Ba_nCu_xO_y$. The first member of this series is identified as BaCuO.

### 3.2. Ultraviolet laser

Fig. 2 illustrates typical TOF mass spectra of positive ions produced by the impingement of laser pulses from a KrF laser (248 nm) with a repetition rate of 10 Hz an laser fluence of 1.2 J $cm^{-2}$ on the surface of a YBCO pellet. The spectra are obtained with the reflecting detection mode both in vacuum (a), and in oxygen (b) with the nozzle aligned perpendicular to the spectrometer axis.

In vacuum all of the atomic components of the target are observed, i.e., Cu, Y, and Ba. In addition to those, a few other species appear such as $O_2$, $YO_2$, and multiply ionized ions with masses between 20 and 50 amu. Furthermore a peak at $M \approx 190$ amu appears, which has been identified as most likely being $Cu_2O_4$.

The introduction of oxygen by the nozzle results in several alterations in the mass spectra. The mass of the observed species ranges between 63 and 165 amu and includes the atomic species Cu and Ba, and the monoxides YO and BaO. Note that the experimental conditions are similar to those used for the deposition of thin films. The only difference is that instead of having the oxygen gas diffused at the same partial pressure throughout the volume of the deposition chamber, it is introduced by the nozzle near the plume region.

### 3.3. Negative ions

By changing the polarity of several components of the experimental apparatus such as that of the acceleration field and the detection system, the TOF spectra of anions are acquired. The ablation of the target occurred in the presence of oxygen supplied by the pulsed nozzle and the data are collected with the reflecting detection system. The spectra contain only low-mass species in both cases of the ablating lasers (the infrared and the ultraviolet one). In general the intensity of the anions is significantly lower than that of the cations (i.e. a factor of $\sim 500$). The most intense peaks correspond to singly and doubly charged atomic and molecular oxygen, although very small amounts of $Cu^-$ are observed. In the case of the excimer laser we could also measure traces of $CuO^-$. (Because these spectra are very simple we do not present them in a separate figure.)

### 3.4. Two-laser experiment

In order to investigate gas phase photodissociation of the plasma components, a two-laser experiment has been performed. The YBCO target is irradiated at an angle of 45° with the infrared (Nd:YAG) laser in vacuum. The ultraviolet (KrF excimer) laser is fired at a later time $\Delta\tau$ that varied between 0 and 40 $\mu$s. The KrF laser beam is parallel to the surface of the target and at a distance of ~0.5 mm away from the ablation point. The delay time used for the application of the pulsed acceleration field remains constant at 70 $\mu$s; this value is the optimal one for obtaining the maximum ion signal.

Preliminary TOF spectra of the cations recorded with the excimer laser firing at several different time delays are presented in Fig. 3. The data obtained with the KrF laser firing with a time delay greater than ~10 $\mu$s and without firing are almost the same. These spectra are characterized by (1) the presence of large-mass clusters, (2) the absence of atomic Cu, and (3) the good resolution of Ba and BaO peaks. When the KrF laser is pulsed almost simultaneously ($\Delta\tau \sim 0$ $\mu$s) with the Nd:YAG laser, only small-mass species are detected. A peak due to Cu appears and the Ba and BaO peaks broaden and overlap. As $\Delta\tau$ increases, species with larger mass begin to appear and the Ba and BaO peaks begin to separate, resembling the case without the KrF laser.

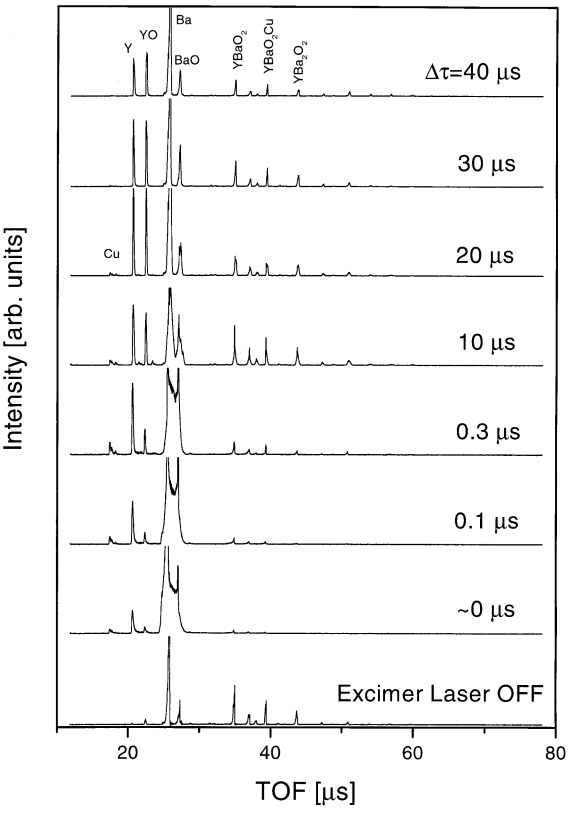


Fig. 3. TOF spectra of positive ions produced by the ablation of a YBCO target in vacuum using a two-laser arrangement. In addition to a Nd:YAG (1064 nm) laser beam that was focused on the target, a KrF (248 nm) laser beam, passing parallel and ~0.5 mm in front of the surface, was synchronized to pulse $\Delta\tau$ ($\mu$s) after the ablation laser.

## 4. Discussion

This study has focused on positive ions as they are considered to be representative of the composition of the species in the plume. The cations are produced either by photoionization of neutral species in the gas phase or by direct emission from the target.

In order to analyze the TOF mass spectra the dependence between mass ($M$) and time of flight ($t$) is approximated by the relation $M = a + bt + ct^2$, where the coefficients $a$, $b$, and $c$ are instrumental constants. The coefficients of the calibration relation are determined using the position on the TOF axis of peaks of elements and their oxides such as Y, YO, Ba, and BaO, that can be identified with certainty. Following the transformation of the TOF axis to mass axis, the identification of peaks associated with large-mass species is carried out using the method of isotopic analysis. Elements such as Cu and Ba have two an seven isotopes, respectively, and therefore, the shape of the peaks is indicative of the presence of these elements and their combinations.

The data shown in Figs. 2 and 1 indicate that short wavelength laser irradiation (248 nm) generates a plasma of mostly elemental and monoxide cations, whereas long wavelength laser irradiation (1064 nm) results in the emission of heavy particles in addition to the light ones. The characteristics of the pulsed laser

beams of both wavelengths used, such as the fluence, the pulse width and the repetition rate, are similar. The difference in the observed mass spectra can be attributed to the difference in photon energy between the two laser sources. Each photon emitted by the KrF excimer laser has an energy of 5 eV. This energy is sufficient to directly ablate atomic and/or molecular species from the target, and in the case, that large clusters are emitted from the target or formed by recombination in the plasma, it is large enough to cause direct dissociation of them in the gas phase. The photons emitted by the Nd:YAG are much less energetic ( $\sim$ 1 eV/photon). Therefore, it is expected that (1) the heating of the surface of the target is thermal-like, which results in micron-sized particles being forced out of the target into the plasma, and (2) the dissociation of these large species in the gas phase is very limited as it requires multiphoton processes.

The mass spectra of the two-laser experiment shown in Fig. 3 lend further support to the explanation given previously. The large-mass species observed in the absence of the KrF excimer laser (Fig. 3), almost completely disappear when the excimer laser interacts with the plume produced by the Nd:YAG laser. The spectra in Fig. 3 for $\Delta\tau \leq 20$ $\mu$s tend to be similar to those shown in Fig. 2, produced by irradiating the target with the KrF laser, i.e. mainly atomic and monoxide species. The broadening of the peaks (especially that of $Ba^+$) can be attributed to the energy release from the photofragmentation of clusters. This suggests that the low mass species observed in the TOF spectra shown in Fig. 2, are the end-products of photodissociation of larger species in the gas phase during the excimer laser pulse (25 ns).

It is interesting to note that in TOF mass spectra of positive ions generated by the Nd:YAG laser and collected using the *reflecting* detection mode, the intensity of the heavy clusters' peaks is significantly reduced and the peaks of the elemental and monoxide positive ions are broadened. This is strong evidence for *metastability* of the large clusters as they travel along the drift tube of the spectrometer. The linear detection system is a velocity-sensitive detector and not suitable to record phenomena of metastability. The reason being that following the spontaneous dissociation of a parent cluster the laboratory velocities of the fragments are almost the same with that of the parents and therefore, they arrive at the detector almost simultaneously. On the other hand, the reflectron is an energy-sensitive detector and therefore, as the fragments have different energies following the dissociation of the parent they will be detected at different times than the parent. This phenomenon of metastability is further investigated presently.

For the initial ablation experiments with the KrF laser, the conventional *linear* detection system was used to collect the TOF mass spectra. The spectra look similar to those reported by Berardi et al. [2]. The peaks are significantly broadened and a uniform background is superimposed to the spectra. The cause of these effects is attributed mainly to the electronically excited neutral species of the plasma, which contribute to the detected signal. The broadening of the peaks is attributed to the neutral species that can be ionized during their residence time in the acceleration region (field ionization). The increase of the spectrum baseline is due to the spontaneous ionization (delayed ionization) of the highly excited neutral species during their flight in the field-free region of the spectrometer, and/or their collisions with the MCP (impact ionization). By using the reflecting detection system these effects can be eliminated from contributing to the spectra.

The negative ions observed in the ablation of YBCO target are almost identical for both laser sources (Sec. 3.3). This is attributed to the fact that negative ions can only be formed in the gas phase by recombination reactions between very slow secondary electrons and neutral species with large positive electron affinities. Among the target constituents, oxygen, copper, and copper oxide have the largest electron affinities: O (1.46 eV), $O_2$ (0.44 eV), Cu (1.23 eV) [8], and CuO (1.78 eV) [9]. As it was mentioned above, the intensity of the anions is significantly lower than that of the positive ions, which leads to the conclusion that the role of the anions in the formation of the film is minor.

There is a distinct difference in the species observed during the ablation of a YBCO target by the excimer laser in vacuum [Fig. 2(a)] and in the

presence of oxygen [Fig. 2(b)]. In vacuum the observed species are mainly elemental cations (i.e. Y, Ba, and Cu), and some minute traces of oxides (e.g. $YO_2$). In the presence of oxygen the observed species are oxides of these elements (YO, BaO, and $Cu_2O$), which are produced by gas phase reactions and in quantities that are comparable to the atomic (Cu and Ba) ones. This difference suggests the following plausible explanation for the different degree of oxygenation and overall quality of thin films deposited under the two different conditions. The oxygen is not absorbed by the film from the ambient but it is transported to the substrate by the oxide species, which upon adsorption react to form films with the correct stoichiometry.

In the case of the Nd:YAG laser ablation with and without oxygen, in addition to the atomic species and their monoxides, large clusters are observed in large quantities. At first, one could think that these large clusters, being derivatives of the YBCO unit cell, would produce good quality thin films. However, one should take into account that these large clusters are stable units—within the time window ($\sim$20 $\mu$s) of the film deposition—and upon adsorption to the substrate it is not favorable for them to be rearranged, leading to an island covered surface. Therefore, the thin films deposited using laser radiation in the infrared region will have bad morphology and poor properties.

## 5. Conclusion

The positive ions formed in the laser ablation of a YBCO target have been investigated. A time-of-flight mass spectrometer and two laser sources of different wavelengths are used to obtain mass spectra in vacuum and in oxygen introduced by a pulsed nozzle near the plasma plume. Choosing the correct detection system makes a difference in observing the true components of the plasma plume. A significant portion of the plasma plume produced by the long-wavelength laser is stable large-mass clusters. These clusters are most likely responsible for the low quality of the films grown using this type of laser source for the ablation of the target. The mass spectra obtained with the short-wavelength laser show that the plasma plume is composed mainly of metal ions and their oxides. We suggest that the formation of the oxides in the gas phase is the way that oxygen is transported to the substrate and incorporated in the film structure.

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